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Microstructural Development of Polycrystalline Alumina Fibers Synthesized from Liquid Precursors

Materials Department
University of California
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13. ABSTRACT (Maximum 200 words) The research of the Office of Naval Research grant at UCSB focused on the research concerns of mechanical properties of fiber reinforced metal matrix composites as well as the understanding of microstructural development in polycrystalline Al ₂ O ₃ fibers synthesized from liquid precursors. It has been closely coordinated with the DARPA/ONR URI program dealing with the design of high performance composites.					
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EXECUTIVE SUMMARY

A. RESEARCH GOALS

The research has been concerned with the mechanical properties of fiber reinforced metal matrix composites as well as the understanding of microstructural development in polycrystalline Al_2O_3 fibers synthesized from liquid precursors. It has been closely coordinated with the DARPA/ONR URI program dealing with the design of high performance composites.

The effort on mechanical properties has focused on the development and validation of models that describe the progression of fatigue cracks in SiC fiber-reinforced titanium composites as well as the effects of such cracks on hysteresis behavior (Walls, McNulty and Zok, 1994). Moreover, the evolution of the interfacial sliding stresses with cyclic sliding has been examined using fiber pullout tests (Walls and Zok, 1994).

The research on fiber development has focused on the effect of Cr_2O_3 and Fe_2O_3 additions on the crystallization behavior, phase transformation sequence, and the evolution of the grain structure in polycrystalline Al_2O_3 materials. Pyrolytic decomposition of Al_2O_3 precursors invariably produces first an ultrafine grained metastable spinal structure (η or γ) which upon further heating to temperatures above $\sim 1000^\circ\text{C}$ transforms to the stable α - Al_2O_3 corundum form. The kinetic preference for γ appears to be significantly influenced by the strain energy associated with the nucleation process. The $\gamma \rightarrow \alpha$ transformation is typically accompanied by extensive grain coarsening, reflecting a combination of relatively sluggish nucleation with an active growth kinetics. Strength optimization in polycrystalline Al_2O_3 fibers requires grain size control in the sub-micron scale, accomplished in practice by "seeding" the precursor with ultrafine α - Al_2O_3 or α - Fe_2O_3 particles. Since the basic

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pyrolytic decomposition sequence ($P \rightarrow \gamma \rightarrow \alpha$) is not altered by seeding, the final grain size is determined primarily by the number density of seeds. An alternate processing route involves adding corundum formers such as Fe and Cr directly to the alumina precursor in the form of soluble salts. The project has emphasized the understanding of the Al_2O_3 grain structure evolution and the underlying thermodynamic and kinetic issues.

B. SIGNIFICANT RESULTS

Under cyclic tensile loading condition, some fiber reinforced titanium composites exhibit *multiple* matrix cracking. Cracking is accommodated by debonding and frictional sliding along the fiber-matrix interfaces, allowing the fibers to remain intact. This process is manifested macroscopically in the form of inelastic strain upon loading and permanent strain upon unloading. Moreover, the retained tensile strength following fatigue is insensitive to the presence of holes or notches or other strain concentrating fractures. In this context, multiple cracking is a desirable feature. However, for structural applications requiring high stiffness and good dimensional stability, cracking is detrimental.

The cracking behavior of the Ti/SiC composites under cyclic loading is closely analogous with the cracking behavior of CMCs under monotonic loading. Recognizing this commonalty, micromechanics models originally developed for CMCs have been modified to account for cyclic loading and used to rationalize the behavior of the Ti/SiC composites (Walls, McNulty and Zok, 1994). Comparisons between experiment and theory show that the sliding stress diminishes with cyclic sliding, a result of wear mechanisms operating within the fiber coating. This trend has been confirmed by independent measurements using fiber pushout testing, as well as cyclic pullout tests conducted on a similar Ti/SiC composite (Walls and Zok, 1994). This reduction in sliding resistance is critical to the tensile response of the composite as

well as to the growth rate of cracks and the saturation crack density. Ongoing studies within the URI program at UCSB are focused on changes in interface properties at elevated temperature and their effects on composite properties.

The research on fiber development has shown that corundum structures can indeed be produced at lower temperatures with finer grain sizes by addition of soluble Cr and Fe salts to the alumina precursors prior to pyrolysis. For example, solutions of Al oxychloride and Cr nitrate with stoichiometry equivalent to $\text{Al}_{1.2}\text{Cr}_{0.8}\text{O}_3$ yield an α structure consisting of platelike grains with low aspect ratio (< 5) and a long dimension on the order of $0.5\ \mu\text{m}$ after heating at 800°C for 1 hr. Similarly, solutions of Al and Fe nitrates with stoichiometries ranging from 10 to 20 mole percent Fe_2O_3 yields equiaxed α structures with average grain sizes on the order of 150 nm after 1 h at 900°C . In contrast, precursors with $< 5\%\text{Fe}_2\text{O}_3$ contain only γ after the same treatment and produce grain sizes $\geq 1\ \mu\text{m}$ when they finally transform at higher temperatures ($\sim 1000^\circ\text{C}$). Compositions between 20 and $50\%\text{Fe}_2\text{O}_3$ synthesized from nitrate precursors yield a mixture of Al_2O_3 - and Fe_2O_3 -rich α phases, as predicted by the equilibrium diagram, with grain sizes consistently on the order of 200 nm. In contrast to previous suggestions in the literature, the nucleation of single phase α in compositions $\leq 20\%\text{Fe}_2\text{O}_3$ appears to occur without the prior formation of Fe_2O_3 -rich "seeds", whereas the partitioned α mixtures exhibit orientation relationships suggestive of epitaxial nucleation of one phase on the other. An alternate hypothesis was proposed to explain the enhancement of the nucleation rate of corundum from γ which promotes grain refinement in polycrystalline Al_2O_3 fibers.

Several transformation paths were identified between the amorphous oxide and the final corundum structure(s). All compositions in the Al_2O_3 - Fe_2O_3 system formed first a metastable spinel (γ) phase, but subsequently showed different transformation paths before arriving to the final microstructure. Compositions with 10

and 20% Fe_2O_3 both formed extended α solid solutions which partitioned only sluggishly at 1100°C. Conversely, powders with compositions above 30% Fe_2O_3 formed an intermediate metastable orthorhombic phase (O) based on the equiatomic AlFeO_3 compound, but also decomposed eventually into the mixture of two α phases. It appears that the α mixture may evolve directly from γ for compositions near 30% Fe_2O_3 , but clearly evolves from the supersaturated α at the lower compositions, and from the O phase as the higher Fe contents. The resistance to partitioning is at a minimum for the 30% Fe_2O_3 , increasing with higher Al_2O_3 content for the α phase, and with higher Fe_2O_3 content (up to 50%) for the orthorhombic phase.

Compositions in the Al_2O_3 - Cr_2O_3 system also formed metastable spinel for Cr^{3+} contents up to ~70 mole%, and appear to devitrify directly to the corundum structure at temperatures as low as 600°C. The differences in behavior appear to be related to the octahedral site preference energy, which increases in the sequence $\text{Fe}^{3+} < \text{Al}^{3+} < \text{Cr}^{3+}$, and its potential influence on the defect vacancy concentration. The pyrolysis atmosphere could also have a significant effect on the transformation rate, but the trends for Fe and Cr are in principle opposite. Reducing atmospheres increase the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio and should promote the spinel form, whereas oxidizing atmospheres increase the $\text{Cr}^{6+}/\text{Cr}^{3+}$ ratio which apparently produces the same effect. No significant evidence could be found, however, of changes in the oxidation state of the cations.

A number of issues emerging from this study can have significant relevance to the microstructural development of fibers. For example, the results suggest the existence of an optimum Fe_2O_3 content for grain refinement, but the mechanism remains to be demonstrated. Further, the evolution of a platelet morphology in the $(\text{Al,Cr})_2\text{O}_3$ compositions offers an interesting opportunity for strengthening if an aligned structure could be developed through processing. Having established a good

conceptual foundation of the problem, it would be highly desirable to continue this research and the related collaboration with 3M.

C. PUBLICATIONS AND PRESENTATIONS

1. Papers

1. "Multiple Matrix Cracking in a Fiber Reinforced Titanium Matrix Composite under Cyclic Loading," by D.P. Walls, J. McNulty and F.W. Zok (in preparation).
2. "Interfacial Fatigue in a Fiber Reinforced Metal Matrix Composite," by D.P. Walls and F.W. Zok, *Acta Metall. Mater.*, **42**, 2675-81, 1994.
3. "Crystallization Behavior and Microstructure Evolution of $(Al,Fe)_2O_3$ Synthesized from Liquid Precursors," A. Polli, F.F. Lange and C.G. Levi, to be submitted to Journal of the American Ceramic Society.

2. Related Presentations

A.G. Evans

July 23, 1992 "Interface Properties for MMCs" and "Overview of UCSB/DARPA Design Issues" 3M Workshop on Metal Matrix Composites.

F.W. Zok

Oct. 28, 1992 "Fatigue Mechanisms in Fiber Reinforced Metal Matrix Composites," Workshop on Modelling of Metal Matrix Composites and Multiphase Materials, Los Alamos National Laboratory (*Invited*) .

Feb. 22, 1993 "Fatigue Mechanisms in Fiber Reinforced Metal Matrix Composites" Symposium on Fatigue of Advanced Materials, TMS Annual Meeting, Denver (*Invited*).

June 2, 1993 "Matrix and Interface Fatigue in Ti-Matrix Composites" Workshop on Titanium Matrix Composites, Materials Directorate, Department of the Air Force, La Jolla (*Invited*).

F.F. Lange

Nov. 1992 ASM Symposium on Composite Materials, Anaheim
 April 1993 American Ceramic Society, Annual Meeting
 June 1993 Woods Hole, ONR Composites Workshop
 Sept. 1993 Composites Workshop, Bordeaux, France

C.G. Levi

March 23, 1993 "Metastable Phase Selection and Microstructural Development during Crystallization at High Undercoolings," invited presentation at the 1993 March Meeting of the American Physical Society, Symposium on Phase Transformations, Seattle, WA.
 Oct. 1st, 1993 "Opportunities for Microstructural Development via Metastable Phases Synthesized at High Undercoolings," invited presentation at the 1993 Congress of the Mexican Academy of Materials, Cancun, Mexico.

D. PARTICIPANTS

1. Students: J. McNulty and A. Polli (fully funded by ONR contract)
2. Post-Docs: J.P.A. Löfvander and M.Y. He (part time)
3. Visiting Professors: V. Jayaram (part time)